CHAPTER IV
RESULTS AND DISCUSSION

Numerous researchers suggested that the Au catalyst could be influenced by many important parameters that include catalyst synthesis condition, reactor operating condition, and storage condition, as explained in Chapter 3. This research work tries to develop the PROX of CO reaction using the Au/TiO_2 catalyst by improving these conditions for the best efficiency of the catalyst. In this chapter, the overall results of the research are shown and discussed into three main parts. The first section shows the optimum condition to synthesize the Au/TiO_2 catalyst with various percentages of metal loading, calcination temperature, and storage condition. This part can suggest the most suitable environment for which to store the catalyst with the least catalytic deactivation from the light. Then, the Au/TiO_2 catalysts were tested the catalytic activity for the PROX reaction with the single-stage reactor processing. For the second part, an optimum prepared Au/TiO_2 catalyst from the first part was applied into the double-stage reactor in order to identify the optimum operating condition for the Au/TiO_2 catalyst in the double-stage reactor processing with various O_2, weight split ratios, and stage temperatures. The final section involves the Au/TiO_2 catalyst activity for the operation with the real composition reformate gas.

4.1 Single-Stage Reactor

4.1.1 Effect of Catalyst Preparation Condition on the Performance of the Catalyst

The first consideration in the development of the PROX of CO reaction in this research is the improvement of the catalyst preparation conditions. Next, the optimum metal loading and calcination temperature of the Au/TiO_2 catalyst prepared by deposition-precipitation was studied for this project. The catalysts with different metal loadings and calcination temperatures were tested with the simulated reformate gas in the single-stage reactor processing. They were tested the catalytic activity in a fixed-bed reactor using 100 mg of catalyst at 80–120 mesh in size. The

reactance gas contained 1%CO, 1%O_2, 40% H_2 with the balance being He at a total flow rate of 50 ml/min under atmospheric pressure.

It is worth noting that the first catalyst preparation is the finding appropriate percentage Au loading on the TiO_2 support. Initially, the percentage of metal loading was varied at 1, 1.5, and 2% of Au/TiO_2 (calcined at 200°C). Figure 4.1a shows the relationship between CO conversion, PROX selectivity, and O_2 consumption versus reaction temperature. It can be found that 1 and 1.5%wt of Au calcined at 200°C gave 100% CO conversion at room temperature (30°C). In addition, 2%wt provided 100% CO conversion at 50°C; therefore, all of samples completely remove the CO contents from the reactant gas at low operating temperature. As a result, the increasing of Au loading could remove CO concentration with 100% at a higher operating temperature, which is in agreement with the work done by Wang et al. (2008). They tested the activity of Au over manganese(II) performance for the PROX reaction with increasing the percent Au loading from 1 to 5.5%. They proposed that complete oxidation of CO could be attained at room temperature over 1% Au/α-Mn_2O_3, the activity of which is notably higher than that of 5.5% metal loading.

For the PROX selectivity term, the 2%wt Au provided the highest selectivity and the lowest O_2 consumption over the tested temperature range. The 1 and 1.5%wt of Au samples provided a slight difference between the PROX selectivity and the O_2 consumption.

Furthermore, the pretreatment condition is an important parameter, which is worth considering for this research wok. The 1%wt Au catalyst was prepared at different pretreatment conditions, which are uncalcined, calcined at 200, and 300°C. The catalysts were tested for the catalytic activity in the single-stage reactor. The catalytic performance shown in Figure 4.1b reveals that the CO conversions were in the order of 200°C > uncalcined > 300°C at 30°C operating temperature. At high operating temperature (80–120°C), the 1%wt Au uncalcined catalyst exhibited the lowest CO conversion.

For the PROX selectivity term, the 1% wt catalyst calcined at 300°C catalyst gave a higher selectivity percentage than the 1%wt Au catalyst uncalcined and calcined at 200°C at the operating temperature range of 30 to 80°C. For the

higher operating temperature, the PROX selectivity of the all samples are slightly different.
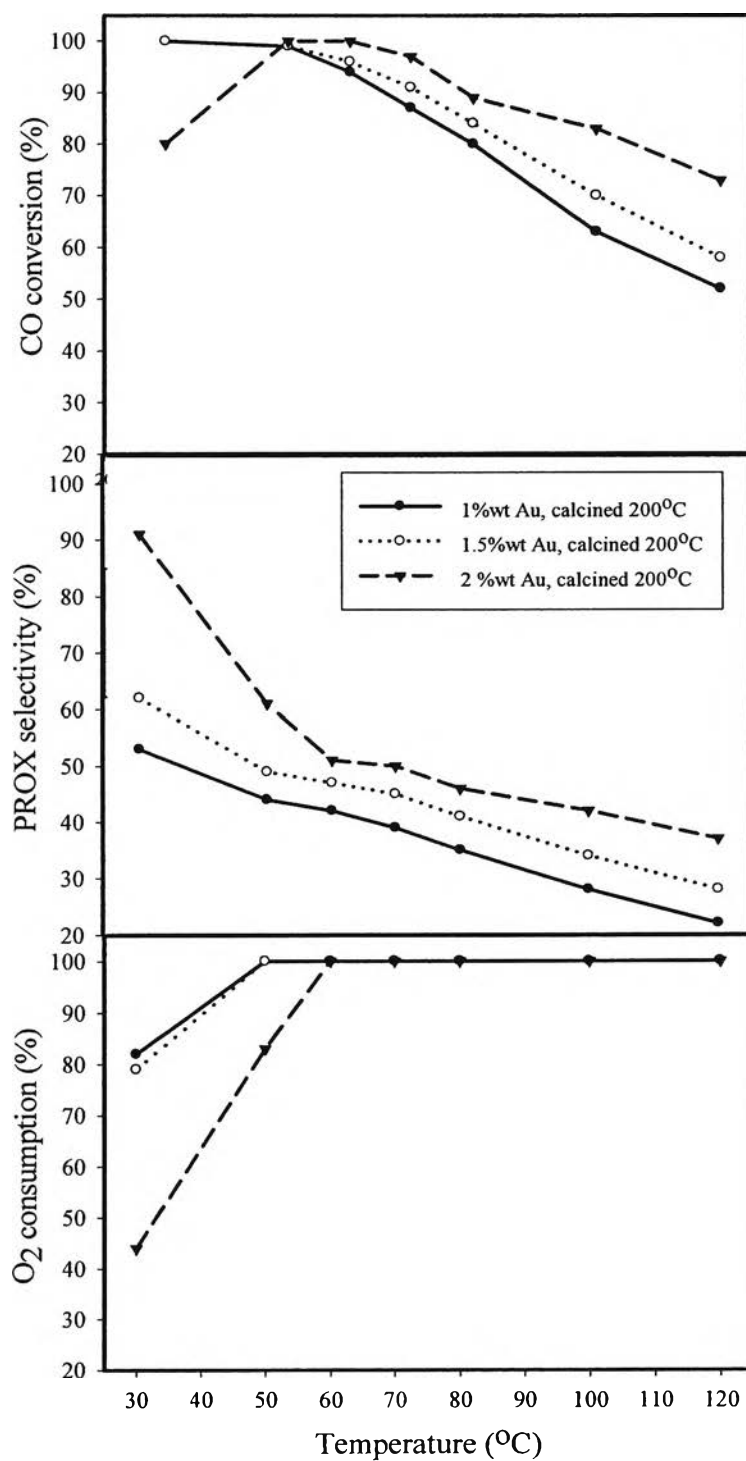

Figure 4.1a Effect of metal loading on the activity of Au/TiO$_2$ catalyst.
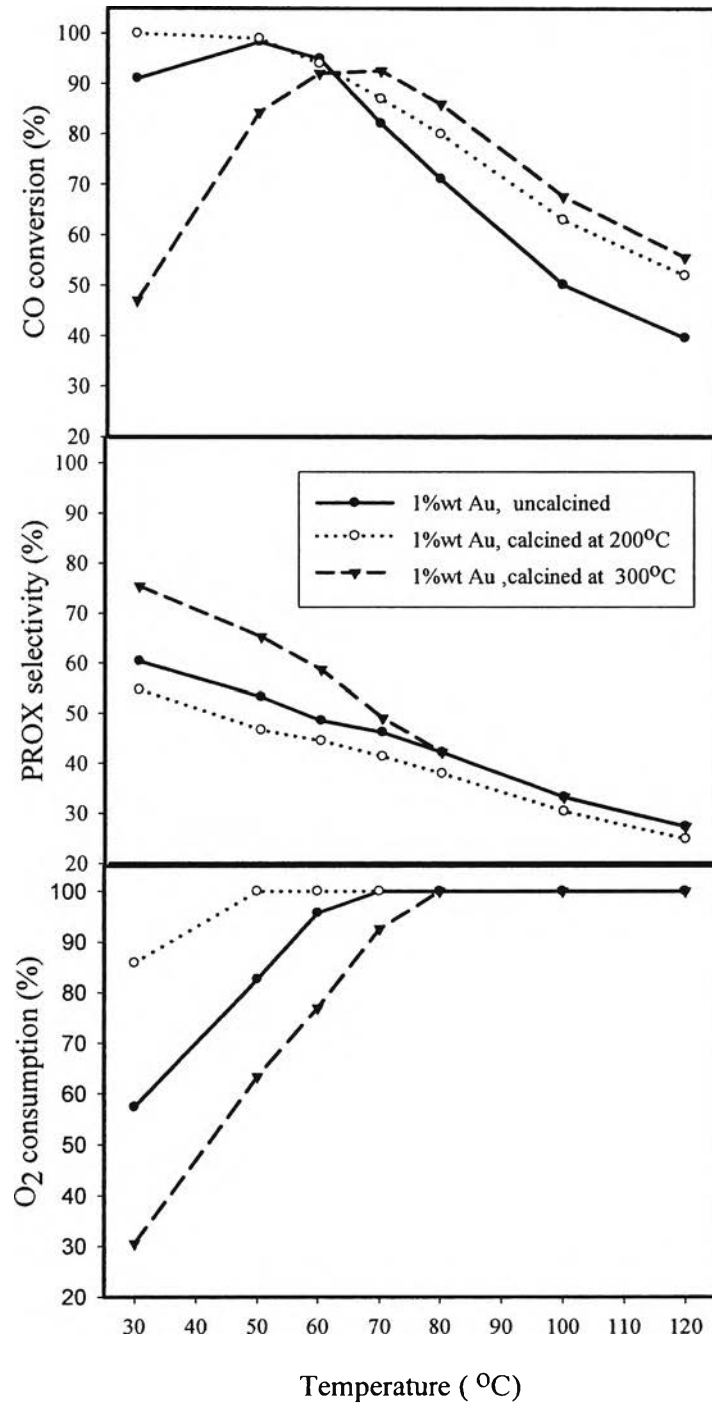
Figure 4.1b Effect of calcination temperature on the activity of Au/TiO₂ catalyst.

Then the actual amounts of Au loading in all prepared catalysts were determined by AAS. Table 4.1 summarizes the expected and the actual values of Au contents in all catalysts, which were prepared by the DP method. The measured percentage of Au loading in the prepared catalysts was much lower than the expected values. The disappearance of Au might be attributed to the error during sample and standard solutions preparation which it is a disadvantage for AAS characterization. The highest actual metal loading of 2%wt Au of Au/TiO$_2$ catalyst calcined at 200°C sample was about 0.82%. This result corresponds with the UV-visible spectrum results shown in Figure 4.2.

Table 4.1 Characterization results of Au/TiO$_2$ catalyst with different metal loadings and calcination conditions

Metal loading (%)	Calcination Temperature (°C)	Actual metal loading (%)[a]	D_{Au} (nm)[b]	Anatase(101) (nm)[c]	X_{CO} (%)[d]
1	200	0.61	3.07	19.10	100
1.5	200	0.77	-	19.47	100
2	200	0.82	3.96	19.05	80
1	Uncalcined	-	-	17.56	91
1	300	-	3.80	19.75	47

[a] Actual percentage metal loading measured by AAS
[b] Au particle size measured from TEM images
[c] TiO$_2$ (P25) anatase (101) crystal size measured by XRD (Scherrer's equation)
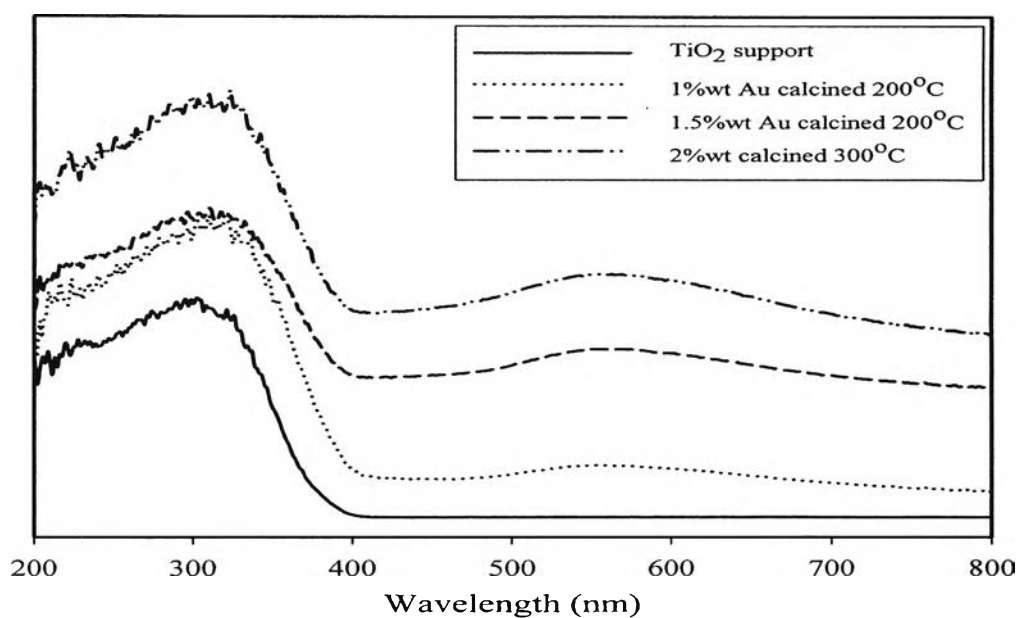[d] CO conversion at 30°C operated in a single-stage reactor with the simulated reformate gas

Figure 4.2 UV-visible spectra of TiO_2 (P25), 1, 1.5, and 2%wt of Au loadings calcined at 200°C.
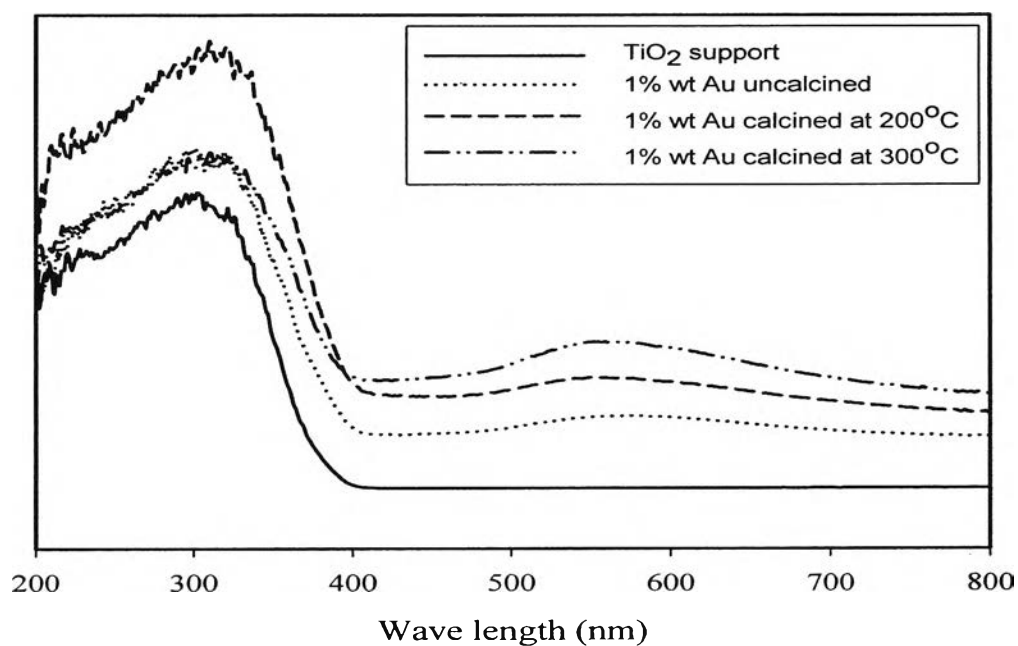

Figure 4.3 UV-visible spectra of TiO_2 (P25) and Au/TiO_2 calcined at different temperatures.

Figures 4.2 and 4.3 display the UV-visible spectra of Au/TiO_2 catalysts with different percentages of metal loading, and calcination temperatures. The spectra of the samples show the adsorption of TiO_2 below 400 nm. The spectra also exhibit another band over 550 nm. This band is the representative of the gold Au^0 nanoparticle quantity (Lee *et al.*, 2007). Apparently from Figure 4.2, the intensity at the band over 550 nm increased with the increasing of metal loading. The AAS results relate to the UV-visible spectrum results that 2%wt Au loading has the highest total metal loading with a maximum quantity of Au^0 presence on the surface of the catalyst following by the 1.5 and 1%wt Au catalysts.

From Figure 4.3, the calcination temperature parameter was studied by increasing the calcination temperature and an evaluation of the amount of Au^0 using the UV-visible spectrophotometer. The result shows that the increase of calcination temperature increased the Au^0 quantity of the catalyst. As shown in the UV-visible spectra, it can be seen that the sample calcined at 300°C has the highest intensity at around 550 nm following by the 1%wt calcined at 200°C and the uncalcined samples. From the result, the increasing metal loading, and the calcination temperature lead to the increasing of content of Au^0 present in the catalyst.

Subsequently, the reduction properties of the catalysts were studied by TPR technique, as shown in Figures 4.4 and 4.5.
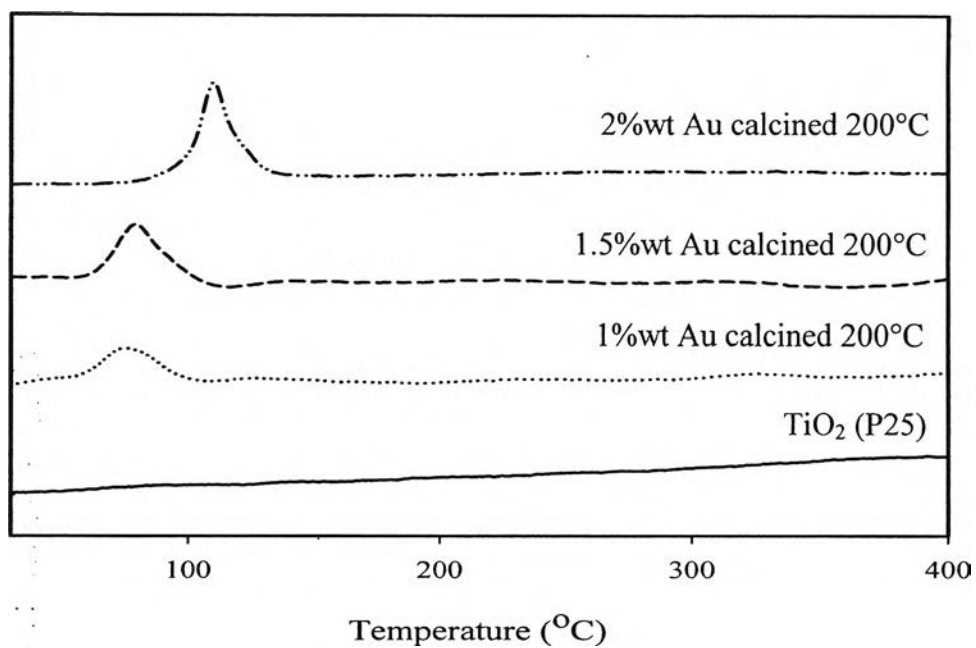
Figure 4.4 TPR profiles of the Au/TiO$_2$ catalysts with different Au loadings.
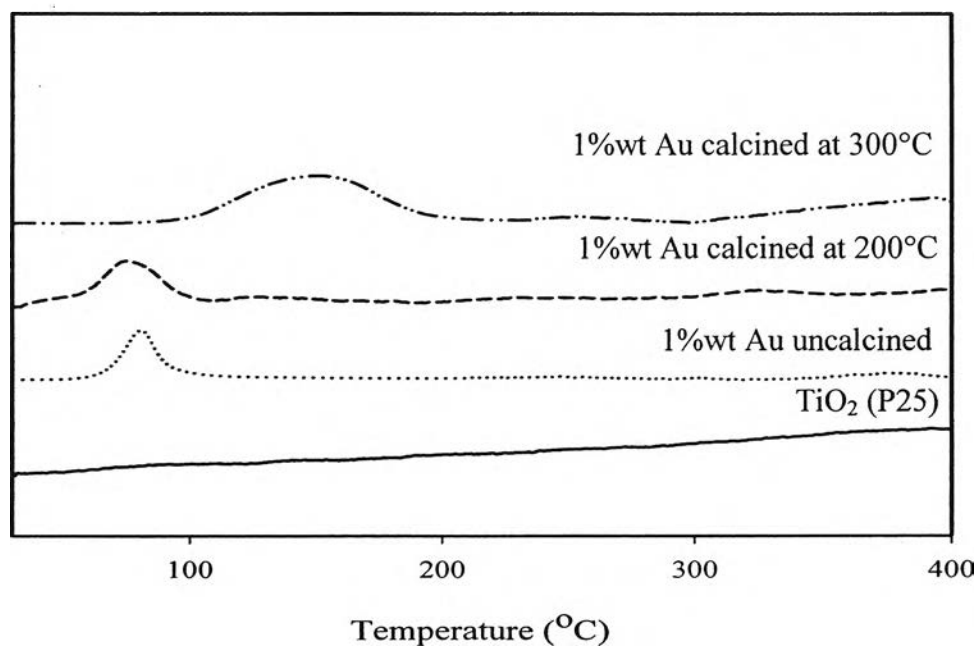

Figure 4.5 TPR profiles of the Au/TiO$_2$ catalysts with different calcination temperatures.

Figure 4.4 shows the TPR results of the 1%, 1.5%, and 2%wt Au catalyst. The 2% wt Au catalyst has the highest intensity, followed by the 1.5%wt and 1% wt Au catalyst, so the 2%wt Au catalyst has the most concentration of Au ions in the catalyst. Moreover, the catalyst with 1% wt Au loadings shows a reduction peak at around 74°C, whereas with the higher metal loading with 1.5% and 2%wt show the peak at 79°C and 108°C, respectively. The different reduction temperature of the Au in each sample can identify the difficulty of the catalyst to be active for any reaction The low temperature of the reducibility respond for the catalytic activity at low temperature (Scire *et al.* 2008). According to the catalytic activity in Figure 4.1a, we can see that the 2%wt Au prefers to be active at a high operating temperature, but the 1%wt Au catalyst prefer to be active at a lower one. This is because the 1%wt Au catalyst has the lowest reduction temperature comparing to the 2%wt sample.

The different calcination samples were tested for reducibility properties with the TPR, as shown in Figure 4.5. All catalysts provided similar intensity of the hydrogen consumption, but they have different reduction temperatures. The 1% wt Au calcined at 200°C has the lowest reduction temperature at approximately 74°C, and gave 100% CO conversion at 30°C. A peak of uncalcined catalyst shows at 81°C, which it is slightly higher than the peak of the Au catalyst calcined at 200°C. This is because the Au uncalcined sample consisted of some contaminants during the preparation step, which was not reduced or calcined. Additionally, the uncalcined sample provided a maximum CO conversion of about 98% at 50°C operating temperature, which is almost the same catalytic activity as the Au catalyst calcined at 200°C for the operating temperature at 50°C. However, TPR result cannot clearly indentify the difference of Au ions preset in the catalysts uncalcined and calcined at 200°C. The Au/TiO_2 catalyst calcined at 300°C has higher hydrogen consumption than the other samples. The calcination can increase the concentration of Au ions in the catalyst because it can generate redistribution on gold by the calcination (Hua et al., 2004). As can be observed from the UV-visible result of the calcination parameter in Figure 4.3 that the concentration of Au^0 increased; therefore, the result of the UV-visible can support the TPR result.

Actually, the increases of the metal loading and the calcination temperature can change the particle size of the Au (Lin and Wan, 2003). As explained in chapter

3, the catalyst with very small gold particle size (<5nm) exhibits impressively catalytic activity at a low operating temperature. Optimum activity is seen with the Au particles at about 5 nm, with a target range of 3 to 8 nm (Hvolback *et al.*, 2007), (Grisel and Nieuwenhuysl, 2001). Then, the 1 and 2% wt Au calcined at 200°C samples were taken TEM images in order to measure the particle size of the catalysts, as shown in Figure 4.6.
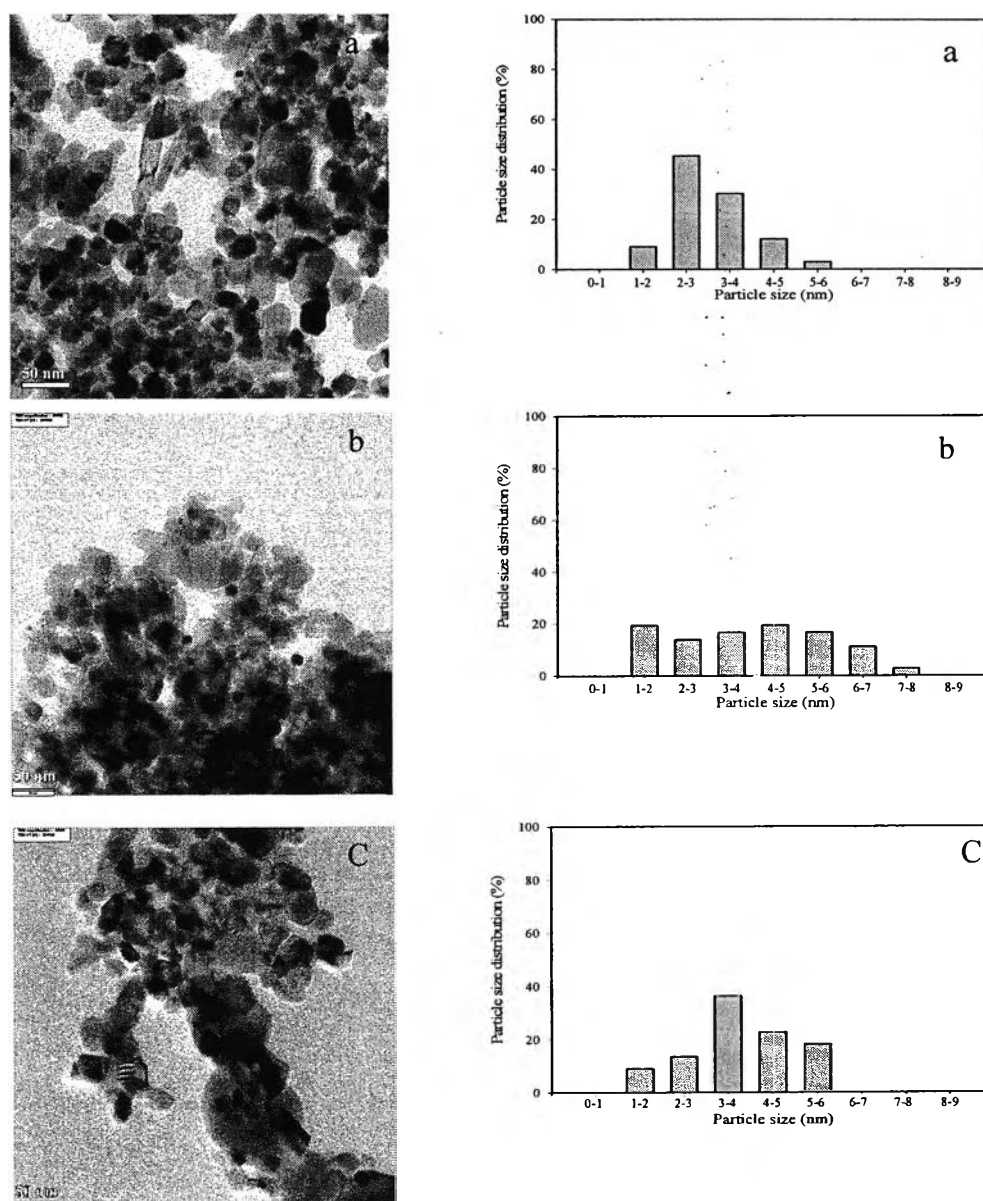

Figure 4.6 TEM images and particle size distribution of Au/TiO$_2$, (a) 1% wt Au calcined at 200°C, (b) 2% wt Au calcined at 200°C, and (c) 1%wt Au calcined at 300°C.

From TEM images in Figure 4.6, we can identify the effect of the increasing percentage of metal loading on the particle size of Au. The average Au particle size of the 1% wt Au catalyst calcined at 200°C is equal to 3.07 nm, as shown in Table 4.1. Then, the average Au particle size growth was increased to 3.96 nm, when the metal loading was increased to 2% wt. Moreover, the particle size distribution of the two samples was compared in Figure 4.6. The trend of particle size distribution also shows that the Au particles grew with the increasing percentage metal loading from 1 to 2%wt. As a consequence, the 1 and 1.5%wt Au catalysts provided better performance at a lower operating temperature than the 2%wt Au catalyst. This is because the Au catalyst with big particle size preferred to be active at high operating temperatures as reported by Boccuzzi *et al.*, (2001) who proposed that the large particle size of Au catalyst has a better performance at a higher operating temperature than the smaller particle size.

The TEM images of Au/TiO_2 calcined at 200 and 300°C are also shown in Figure 4.6. It can be suggested that the average Au particles size and particle size distribution of the Au/TiO_2 calcined at 300°C (3.8 nm) are larger than those calcined at 200°C (3.07 nm) catalysts, as shown in Table 4.1. It can clearly be seen that the Au/TiO_2 catalyst calcined at high operating temperatures can increase the Au particle size due to the agglomerate of the Au. Then, the Au/TiO_2 calcined at 300°C catalyst prefers to be active at a high operating temperature.

However, the increasing of metal loading and calcination temperature did have a strong influence on the support TiO_2 (P25), as seen in XRD results. Figures 4.7 and 4.8 depict the XRD patterns of the Au/TiO_2 with different metal loadings and calcination temperatures. The diffraction peaks are attributed to anatase and rutile phases of TiO_2 (P25) crystal. The peaks of gold are expected at $2\theta = 38.2°$, 44.4°, and 64.4°, but no obvious gold peak was found in the samples (Grunwaldt *et al.*, 1999). The gold particles sizes in the prepared catalysts are too small to be detected by XRD. It was observed that the increasing of metal loading parameter has no effect to the crystallites of the TiO_2. Actually, the catalyst was calcined at only about 200°C, which is too low temperature to change the pattern of the TiO_2 (P25) and the TiO_2 anaste phase is typically transformed into rutile phase at very high temperature approximately 800°C (Mazaheri *et al.*, 2008).

Therefore, it can be seen from Figure 4.8, that the difference in the crystallity of the Au/TiO₂ catalyst when it was calcined at high temperature is not noticeable. Figure 4.8 shows the XRD pattern of the TiO₂ (P25), that as of metal loading. The peak of Au could not be found from the XRD result because the particle size of Au present in the catalyst was smaller than 5 nm (as shown in Table 4.1). In addition, the increasing calcination temperature up to the maximum of 300°C in air did not change the phase of the TiO₂ (P25).
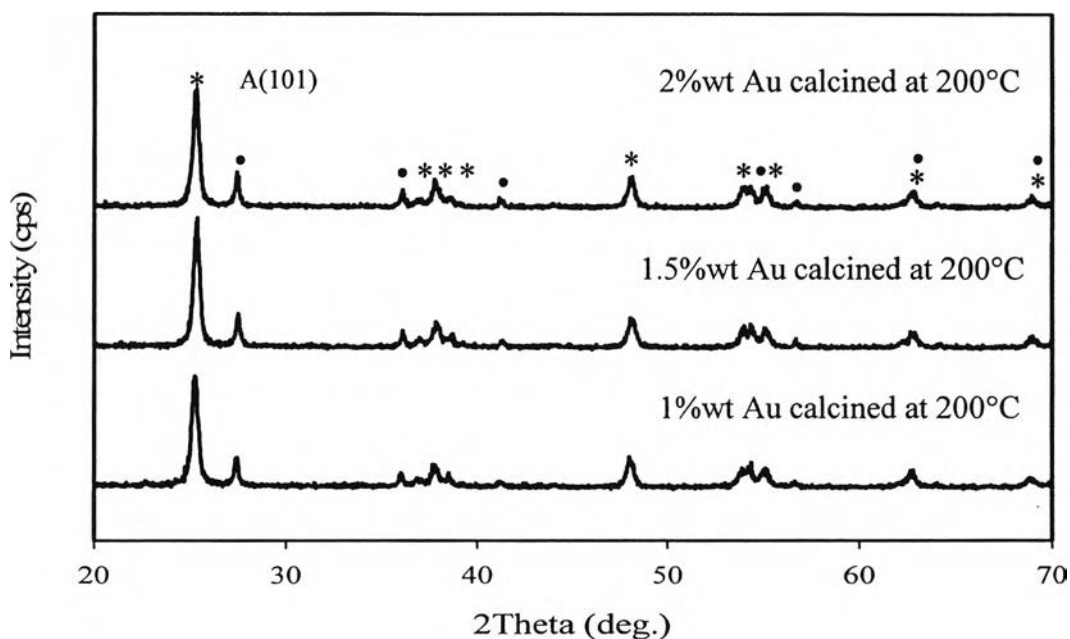

Figure 4.7 XRD patterns of Au/TiO₂ with different metal loadings: Anatase (*) and Rutile (•).
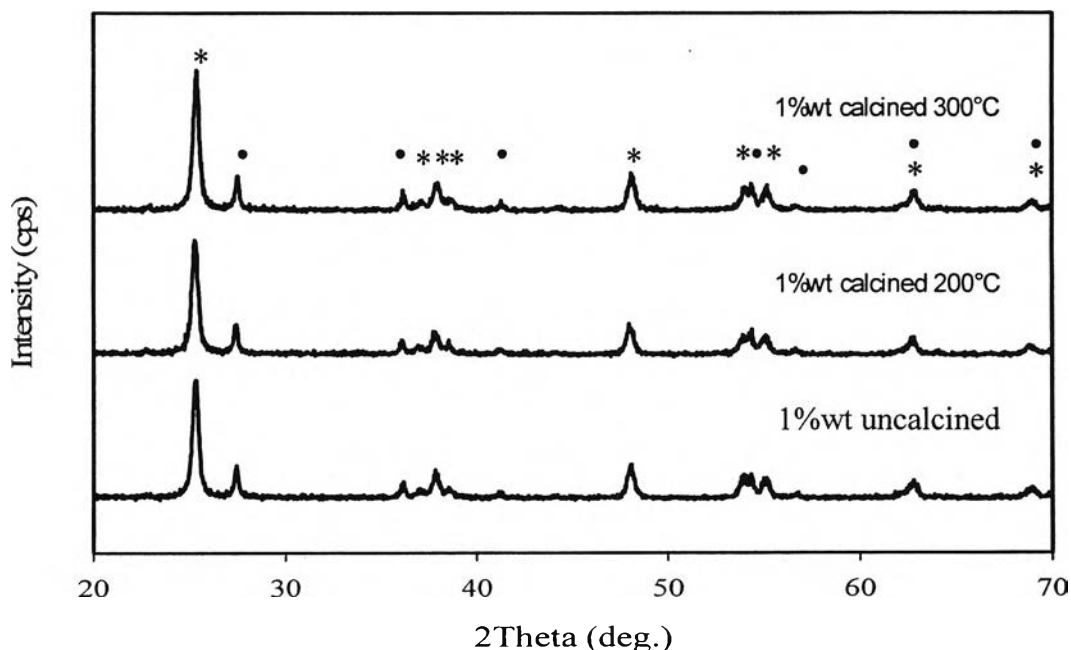
Figure 4.8 XRD patterns of Au/TiO₂ with different calcination temperatures: Anatase (*) and Rutile (•).

4.1.2 Single-Stage with the PROX Reaction

From our focus of study of the preparation conditions of the catalysts, it was noted that the Au/TiO₂ catalyst, with 1% metal loading and calcined at 200°C, is the most efficient and optimum catalyst for the PROX of CO at low operating temperatures. Then, the 1% Au/TiO₂ (P25) calcined at 200°C, was primarily studied to compare the performance of the single-stage and double-stage reactors for the PROX of CO reaction. Beginning with the single-stage reactor, the activity of the Au/TiO₂ catalyst was tested in the temperature range of 30 and 120°C, as shown in Figure 4.9. The Au/TiO₂ catalyst completely removed CO with a maximum PROX selectivity of approximately 54% via the oxidation reaction at 30°C. When the reaction temperature was increased to 120°C, the CO conversion and PROX selectivity were reduced to about 53 and 24%, respectively. In addition, when only TiO₂ support without Au was tested with the PROX of CO reaction in the single-stage at the same range of reaction temperature, it did not show any activity.

Therefore, this result can confirm that Au is the active site of the Au/TiO₂ catalyst for the PROX of CO reaction.
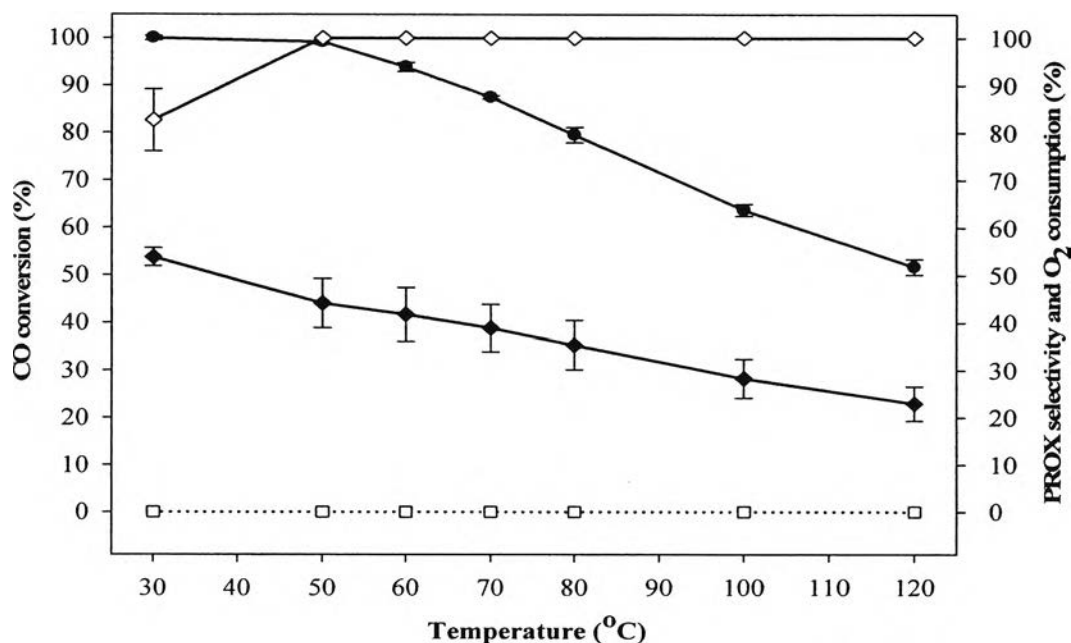

Figure 4.9 Activity of 1wt% Au/TiO₂ and TiO₂ (P25) support calcined at 200°C in a single-stage reactor. Solid line CO conversion (•), PROX selectivity (♦), and O₂ conversion (◊): Dotted line CO (□) of TiO₂ (P25).

4.1.3 Effect of CO₂ and H₂O Concentrations

Firstly, the 1%wt Au/TiO₂ was tested for performance with the simulated reformate gas composition (1%CO, 1%O₂, 40% H₂ and balanced with He), as shown in section (a) of Figure 4.10. The catalyst produced very impressive activity. However, when 10% or 100,000 ppm of H₂O was added into the reactant gas, H₂O had a slightly lower effect on the activity of the catalyst. As shown in Figure 4.10 section (b), the CO conversion dropped to approximately 82%, but the PROX selectivity increased slightly to about 55%. This may be due to the fact that the H₂O blocked the excess to the active site of CO and O₂. These results are in agreement with the findings of Daté and Haruta (2001). They found that the moisture multiplied the catalyst activity 10 times up to 200 ppm H₂O. The role of water is to supply hydroxyl group on the surface of the catalyst, which can support O₂ for the

PROX reaction. This action did not change the mechanism of the reaction; however, when the concentration of H_2O was increased to over 6000 ppm, the activity was depressed due to the blocking of the active sites. For this research, the massive concentration of H_2O with the reactant gas had negative effects on the activity of the catalyst for the reaction.

When, 10% or 100,000 ppm of CO_2 was added into the reactant mixture in order to investigate the deactivation of the catalyst, it could reduce the efficiency of the catalyst for the CO oxidation, as shown in the Figure 4.10 section (c). The CO conversion and PROX selectivity dramatically dropped to around 54 and 20%, respectively. From these results, when comparing the effects of the addition of H_2O and CO_2 in the reactant gas on the performance of the catalyst for the reaction, it was noted that CO_2 has more disadvantages for the catalytic activity than H_2O. This is because the carbonate specie blocked the active sites of the catalyst. Luengnaruemitchai *et al*. (2004) used Au/CeO_2 catalyst for the PROX by increasing the CO_2 concentration in the feed stream from 2 to 20%. They found that the CO conversion dropped from 92 to 85%. For the selectivity, it received little impact from the presence of CO_2 in the reactant gas. Steyn *et al*. (2007) studied the activity of Au/TiO_2 as a catalyst in the presence of CO_2 in the reactance gas mixture, and found that the percentage of CO conversion reduced to around 8%.

Finally, 10% of CO_2 and 10% of H_2O were added to the reactant in order to study the effects of the combination of the both component presences on the activity of Au/TiO_2. From Figure 4.10 (d), the results showed that the ability for removing CO concentration rose to approximately 70%. The CO_2 intermediate can be decomposed by H_2O (Daté *et al*., 2004). H_2O reacts with the carbonate (possibly via $CO_3 + H_2O \rightarrow CO_2 + 2OH$) to generate OH- species at low operating temperature (Schumacher et al., 2004). Moreover, some positive effects from H_2O are more dominant than the negative effects of CO_2. H_2O can enhance WGS reaction and promote some OH- species (Simsek *et al*., 2007, Daté and Haruta, 2001). Therefore, the catalytic activity trend becomes good for the combination feeding of H_2O and CO_2 with the reactant gas.
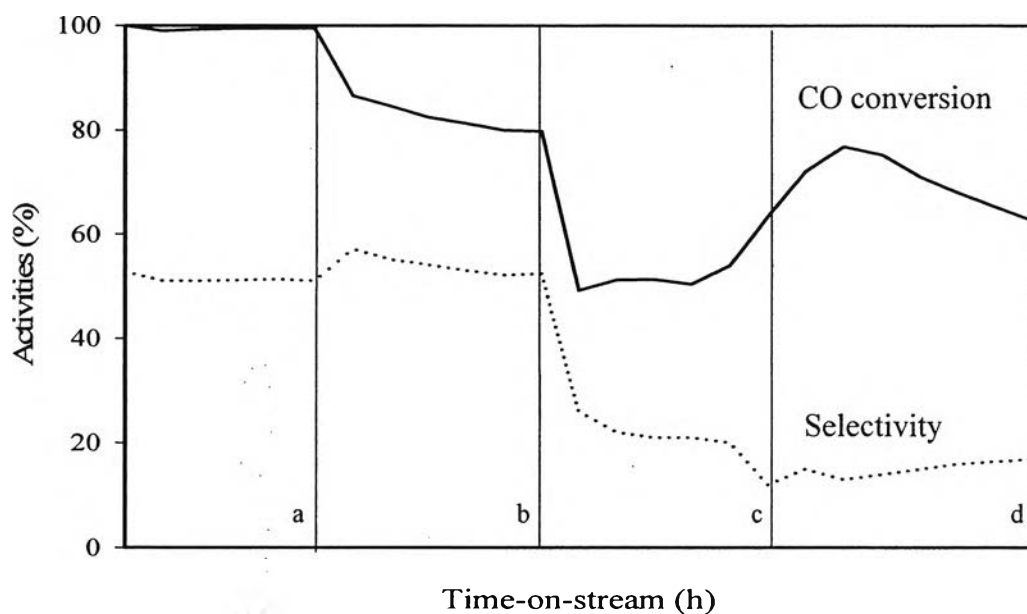
Figure 4.10 Effect of CO_2 and H_2O concentrations in the reactant gas over the Au/TiO$_2$ catalyst. Reactant composition: (a) simulated reformate gas, (b) 10% H_2O, (c) 10% CO_2, and (d) 10% CO_2 + 10% H_2O.

4.1.4 Storage Influence on the Activity of the Catalyst

Many researchers proposed that the Au/TiO$_2$ catalyst is very sensitive to the light. The light can affect the structure, particle size, and performance of the catalyst. Therefore, in this research work, we attempted to study the possibility of the deactivation of the catalyst under the light. The catalyst was kept in two different environments for 1, 2, and 3 months (exposed and unexposed to a light source) in order to evaluate the influence of light on the performance of the catalyst for the PROX. The activity of the fresh catalyst and sample exposed to the light were compared in the single-stage reactor, as shown in Figure 4.11.
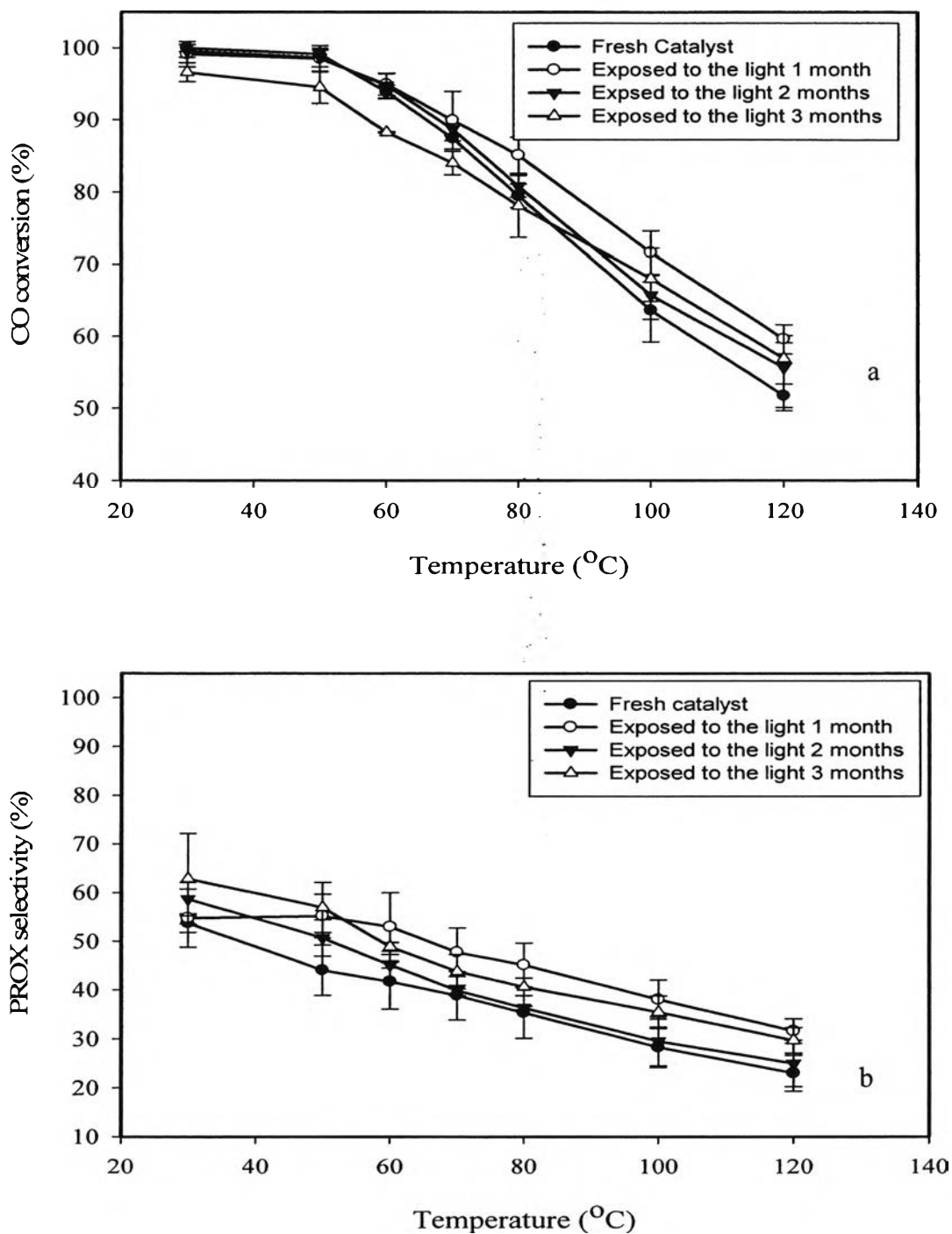
Figure 4.11 Activity of Au/TiO₂ catalyst with different storage conditions: (a) CO conversion, and (b) PROX selectivity.

From Figure 4.11a, all storage conditions (except at 3 months) exposed to the light provided almost the same CO conversion for the reaction at a low operating temperature (30–70°C). At the low operating temperature, it can clearly be seen that the deactivation of the sample occurred on the one exposed to the light for 3 months because it provided lower CO conversion than the other samples. At the higher operating temperature (100–120°C), the catalysts exposed to the light seem to be slightly more active than the fresh catalyst. Moreover, the exposed to the light catalyst has a PROX selectivity higher than the fresh catalyst, as shown Figure 4.11b.

The TPR results reveal that the catalyst exposed to the light for 3 months has the lowest Au ion intensity, as shown in Figure 4.12. We notice that the exposed catalysts have lower Au ion intensity than the fresh catalyst. This indicates that the light has an ability to reduce Au ion on the surface of the catalyst, and Au may migrate into the bulk TiO_2 during storage (Lee $et\ al.$, 2007). This result can be supported by UV-visible result, as shown in Figure 4.13. The fresh catalyst has some Au^0 concentration present on the surface of the Au/TiO_2 catalyst. The sample exposed to the light for a month. After that, it was tested with the UV-visible to evaluate the quantity of Au^0 present on the surface of the catalyst, and (Figure 4.13) showed slight increase of Au^0 due to the reduce of Au ion by the light. According to TPR result in Figure 4.12, it shows a reduction peak of Au ion for the sample exposed to the light for 1 month at approximately 62°C which is significant smaller than the reduction peak of Au ions of the fresh catalyst. For the catalysts exposed to the light for longer period 2 and 3 months, the TPR results are shown in Figure 4.12. The Au ions reduction peak of the both samples became smaller when they were exposed to the light for a long time. Furthermore, the UV-visible results of the 2 and 3 month light expos are show not much difference of the Au^0 concentration present on the surface of the catalyst from the one exposed to the light for only 1 month, because some of Au^0 on the surface migrated into the pore of support.

TEM images indicate that light has influence on the particle size, as shown in Figure 4.14. The catalyst exposed to the light has an average particle size bigger than the fresh catalyst, as shown in Table 4.2. Moreover, the particle size distribution trend (Figure 4.14) is bigger when the catalyst was exposed to the light

for 1, 2, and 3 months. Furthermore, since Au is very sensitive to the light, the catalyst exposed to the light for over 3 months has a bigger particle size of about 0.66 nm which is larger than the catalyst storage in the dark bottle. The light is capable of reducing the Au, and have a possibility of sintering the Au(III). Owing to the larger particle size of the catalyst, the catalyst exposed to the light for 1, 2, and 3 months is more active than the fresh catalyst at the high operating temperature, as shown in Figure 4.11.
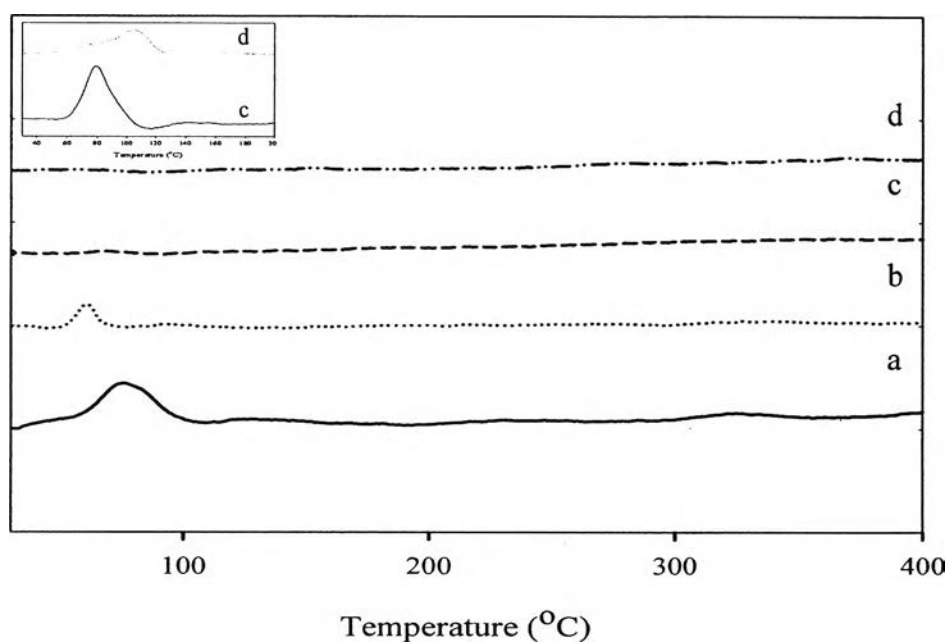

Figure 4.12 TPR profiles of Au/TiO$_2$: (a) fresh catalyst, (b) exposed to light for 1 month, (c) exposed to light for 2 months, and (d) exposed to light for 3 months.

Table 4.2 Characterization results of 1%wt Au/TiO$_2$ 200°C calcined catalyst with different storage conditions

Storage condition of the catalyst	D$_{Au}$ (nm)[a]	Anatase (101) (nm)[b]	X$_{CO}$ (%)[d]
Au/TiO$_2$ fresh	3.07	19.10	100
Au/TiO$_2$ exposed to the light 1 month	3.17	22.06	99.1
Au/TiO$_2$ exposed to the light 2 months	3.49	21.75	99.5
Au/TiO$_2$ exposed to the light 3 months	3.73	21.31	96.6

[a] Au particle size measured from TEM images
[b] TiO$_2$ (P25) anatase (101) crystal size measured by XRD (Scherrer's equation)
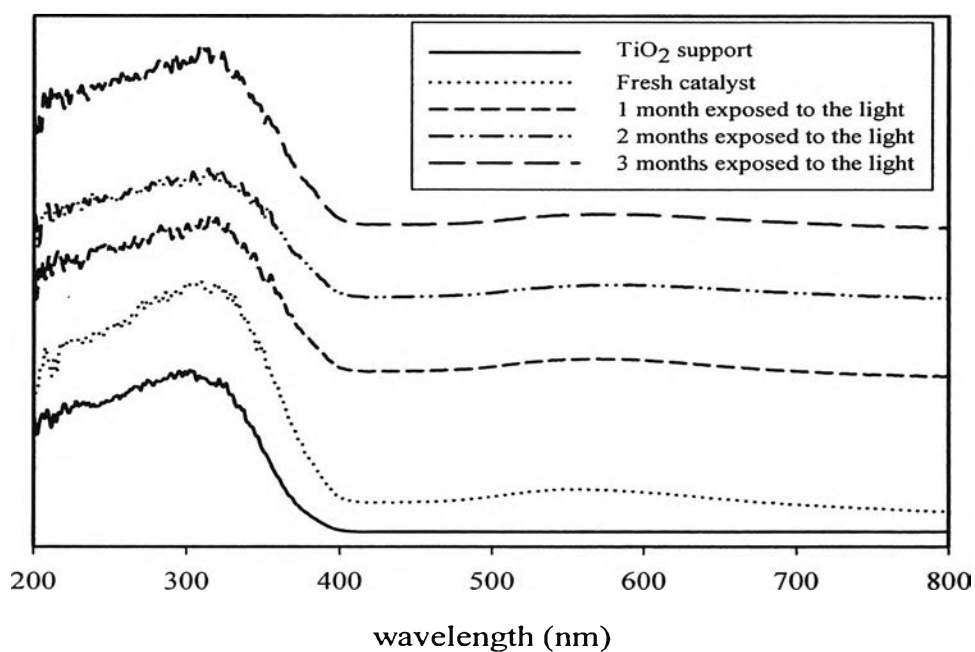[c] CO conversion at 30°C operated in a single-stage reactor with the simulated reformate gas

wavelength (nm)

Figure 4.13 UV-visible spectra of TiO$_2$ (P25) and Au/TiO$_2$ with different storage conditions.
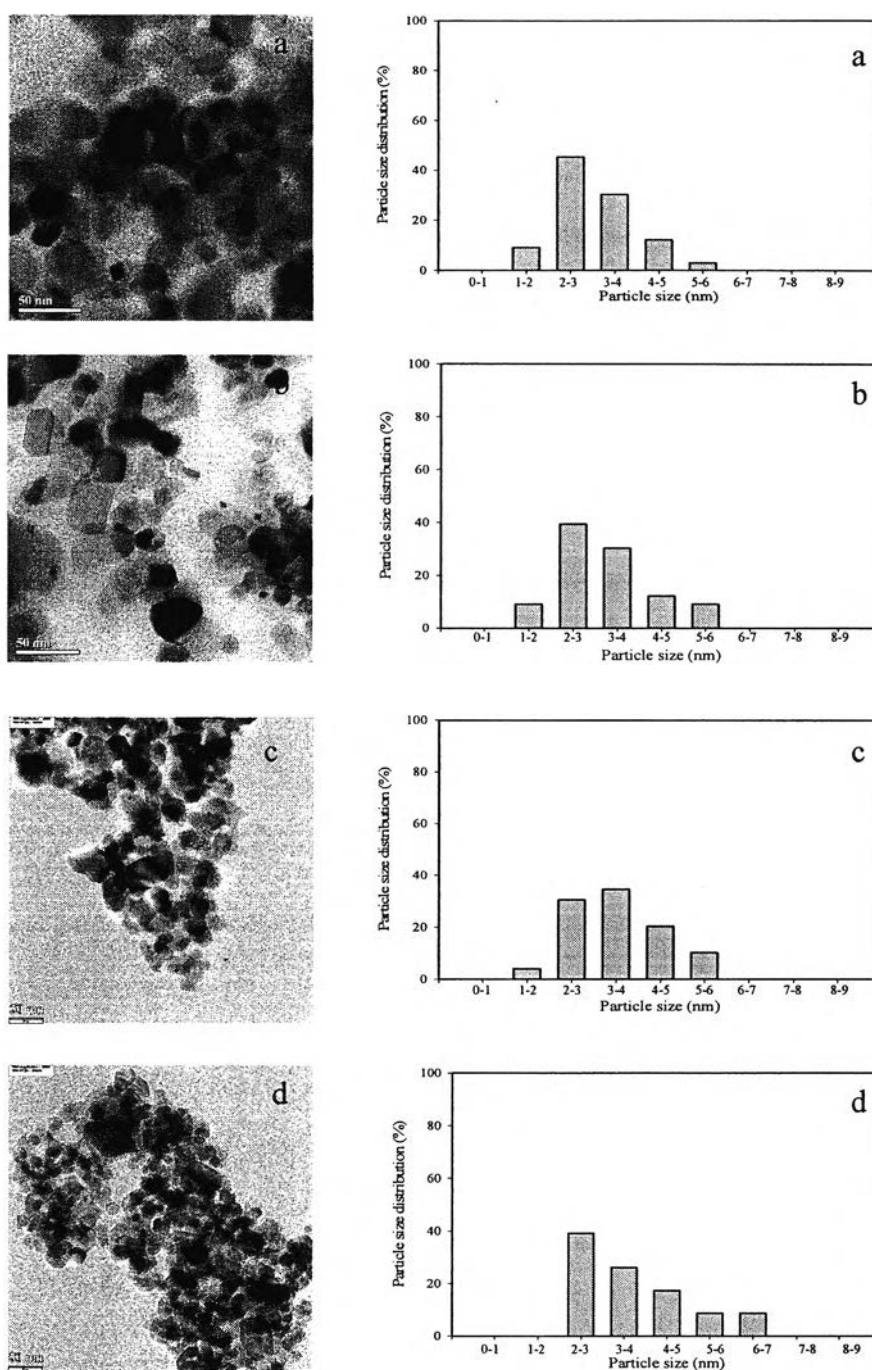
Figure 4.14 TEM images and particle size distribution of Au/TiO_2: (a) fresh catalyst, (b) exposed to light for 1 month, (c) exposed to light for 2 months, and (d) exposed to light for 3 months.
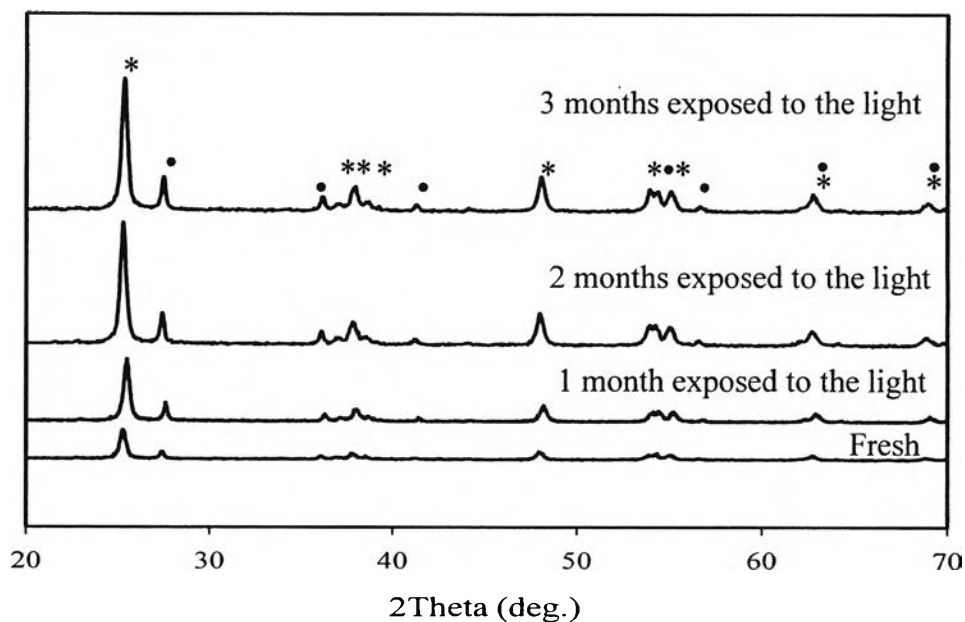
Figure 4.15 XRD patterns of Au/TiO$_2$ with different storage conditions: Anatase (*), and Rutile (•).

The catalysts with different storage conditions were tested for the XRD, as shown in Figure 4.15. The anatase and rutile forms of titania were observed. The position of XRD peaks 2θ of the all samples were of similar pattern. It was observed that for the longer storage, the diffraction of titania becomes shaper because the light could modify the titania to more crystallinity and give large crystallite size, as shown in Table 4.2. There was no evidence of Au peak on the XRD result because the Au crystalline size was smaller than 5 nm.

4.1.5 Stability of the Catalyst

The Au/TiO$_2$ catalyst was tested for stability with the PROX of CO at 30°C for 60 hours, as shown in Figure 4.16. From the results, the catalyst shows poor stability in activity during the tested time. The catalyst provided 100% CO conversion for only 8 hours. After that, the percentage of CO conversion significantly dropped to 70% after 60 hours. The deactivation of the catalyst during the reaction is caused by the accumulation and deposition of by product on the catalyst surface (Schumacher et al., 2003).
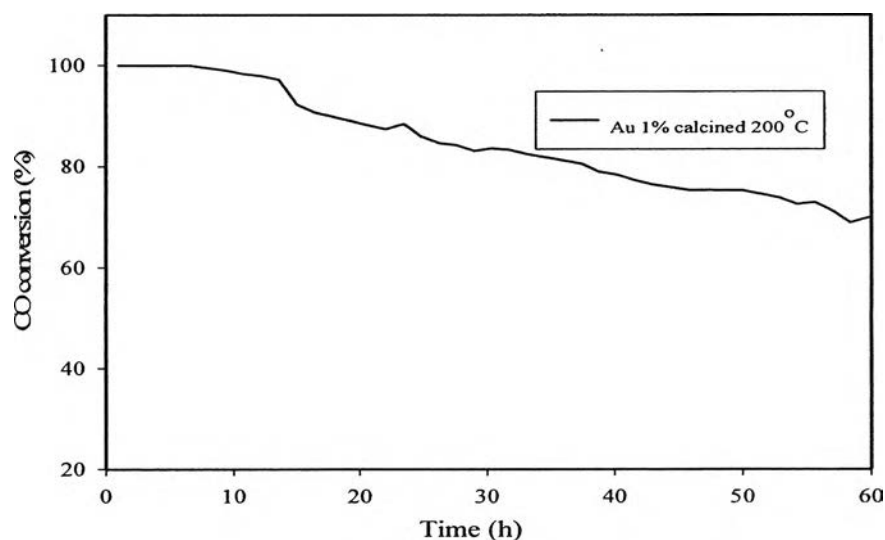
Figure 4.16 Stability of the Au/TiO_2 catalyst.

4.2 Double-stage Reactor

4.2.1 Influence of O_2 Split Ratio of Double-Stage Reactor on the Process Performance

Another method used to improve the PROX of CO oxidation from the simulated reformate gas is to operate in the double-stage reactor. The optimum O_2 spit ratio between both reactors is the first parameter for improving the process performance. Because of similar reactor temperatures with different O_2 split ratios, results could provide various process performances, as shown in Figure 4.17. The temperature of both reactors were fixed at 30°C and the O_2 split ratios were varied at 20:80, 40:60, 50:50, 60:40, and 80:20. From Figure 4.17, the O_2 split ratios at 20:80, 50:50, and 80:20 provided the highest CO oxidation approximately 90%. However, the highest percentage of PROX selectivity is given roughly 80% by the O_2 split ratio at 50:50. Therefore, an optimum O_2 split ratio is 50:50.
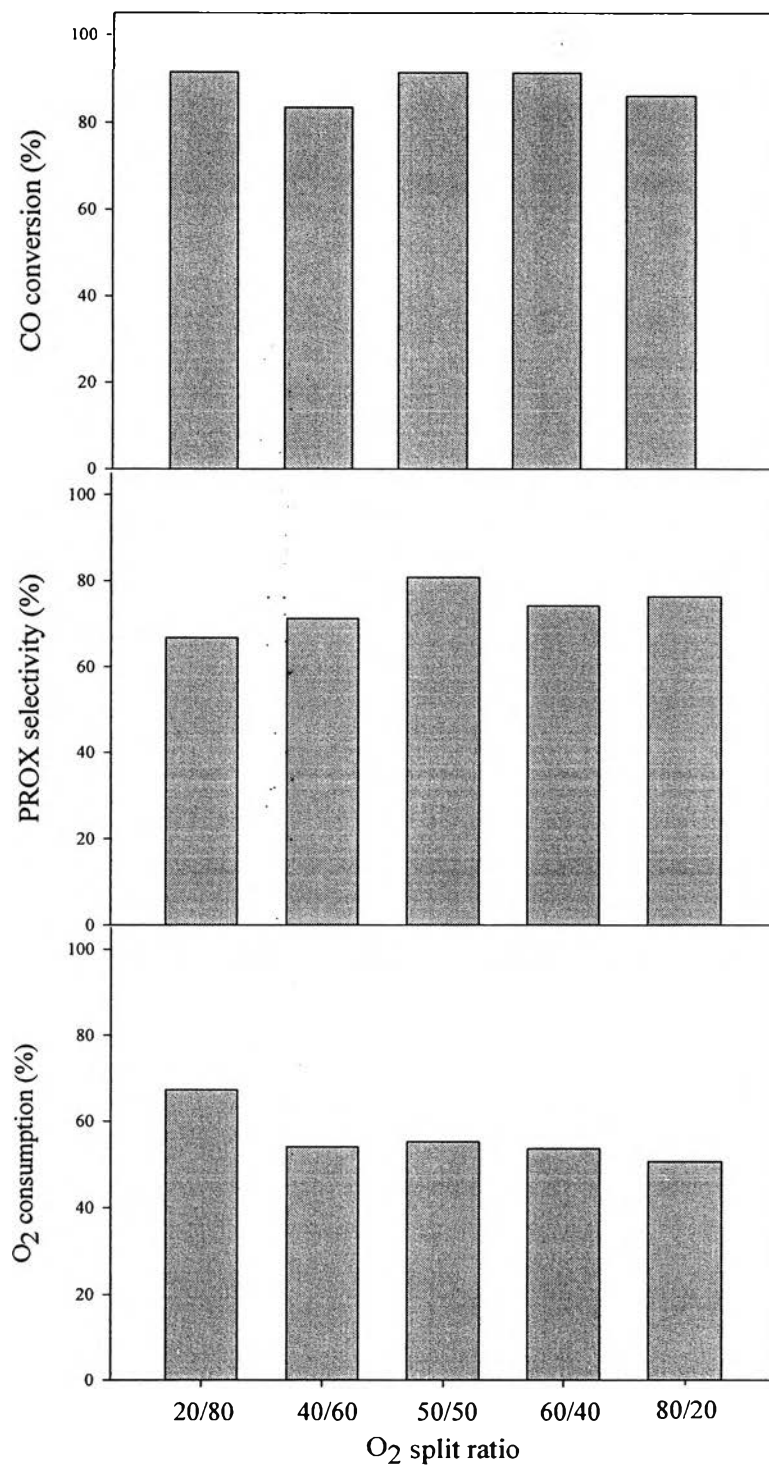
Figure 4.17 Catalytic activities of 1% Au/TiO₂ calcined at 200°C in a double-stage reactor with various O₂ split ratios at a reaction temperature of 30°C.

However, Srinivas and Gulari (2006) operated double-stage reactor for the PROX of CO reaction by $Pt/\gamma-Al_2O_3$, and found that the highest CO conversion of 99.88% was obtained at the O_2 split ratio of 60:40.

4.2.2 Influence of Stage Temperature of Double-Stage Reactor on the Process Performance

The temperature of both reactors is also an important parameter that has an influence on the process performance. The Au/TiO_2 catalyst was tested in the double-stage reactor with a fixed O_2 split ratio of 50:50, with various temperatures of the first reactor from 30 to 120°C and a fixed temperature of the second reactor at 30°, 50°, 80°, 100°, and 120°C, as shown in Figure 4.18. The points which provided the highest CO conversion are at 30°C at the first stage temperature, and fixed the second stage temperature at 30 and 80°C. Furthermore, if considering on the PROX selectivity, when the stage temperature was fixed at 30°C for both reactors and 30°C at the first reactor and the second stage temperature at 50°C, both conditions provided the highest over 80% PROX selectivity. At high temperatures (80–120°C), it is seen that the double-stage reactor shows higher percentage of PROX selectivity than the single-stage in all conditions. From the results, it can be concluded that the 30°C temperature of the first and the second stages gave the best performance.
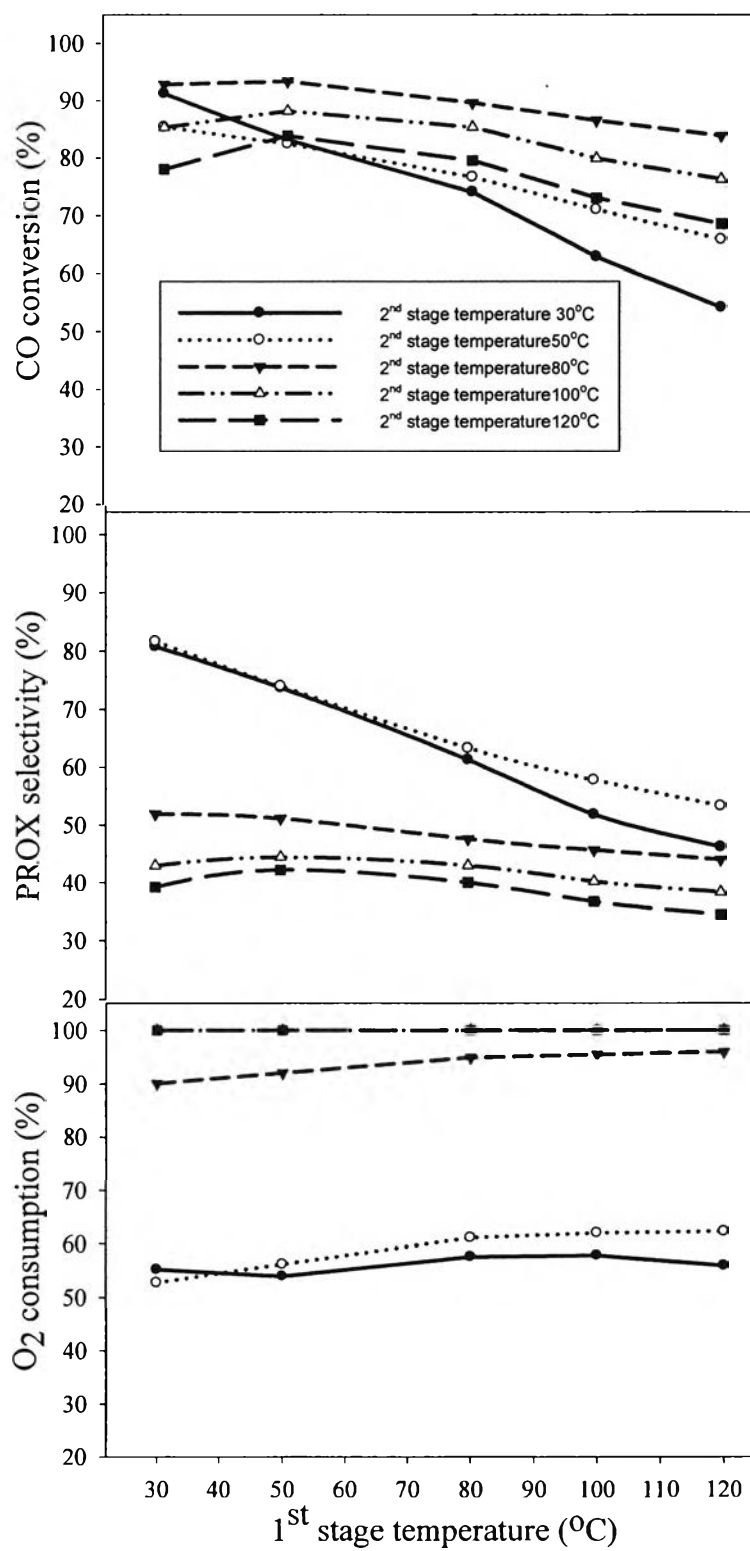
Figure 4.18 Au/TiO$_2$ catalyst activities with various reactor temperatures in a double-stage reactor at an O$_2$ split ratio of 50:50.

4.2.3 Influence of Weight Split Ratio of Double-Stage Reactor on the Process Performance

The weight of the catalyst in each reactor is the last important parameter, to influence the activity of the catalyst for operating in the double-stage reactor. The first and second reactors were split with the weights as 20/80, 40/60, 50/50, 60/40, and 80/20. They were then tested for the catalytic activity for the PROX reaction in the single-stage reactor processing (as shown in Figure 4.19). For the CO conversion, the catalyst with the weight split ratio at 50/50 provided the highest activity. In addition, the weight split ratio at 40/60 and 60/40 gave slightly different CO conversion results. For the PROX selectivity, it seems that when the weight of the catalyst in the first stage increased, the percentage selectivity also rose. The weight split ratio at 80/20 exhibited the highest PROX selectivity, but this weight split ratio gave the lowest CO conversion. Therefore, the optimum for the weight split ratio is at 50/50 because it provided the highest CO conversion and high PROX selectivity over 80%.
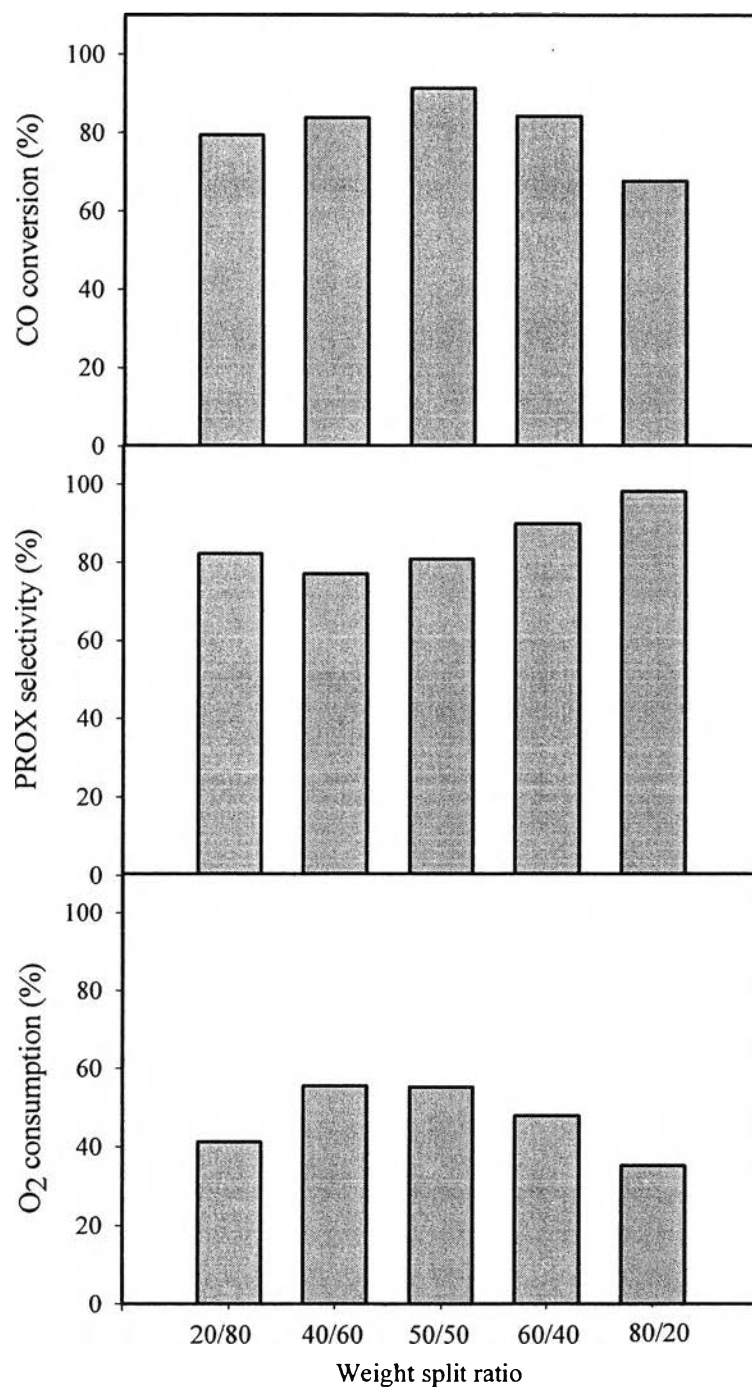
Figure 4.19 Catalytic activities of 1% Au/TiO$_2$ calcined at 200°C in a double-stage reactor with various weight split ratios at a reaction temperature of 30°C and an O$_2$ split ratio of 50:50.
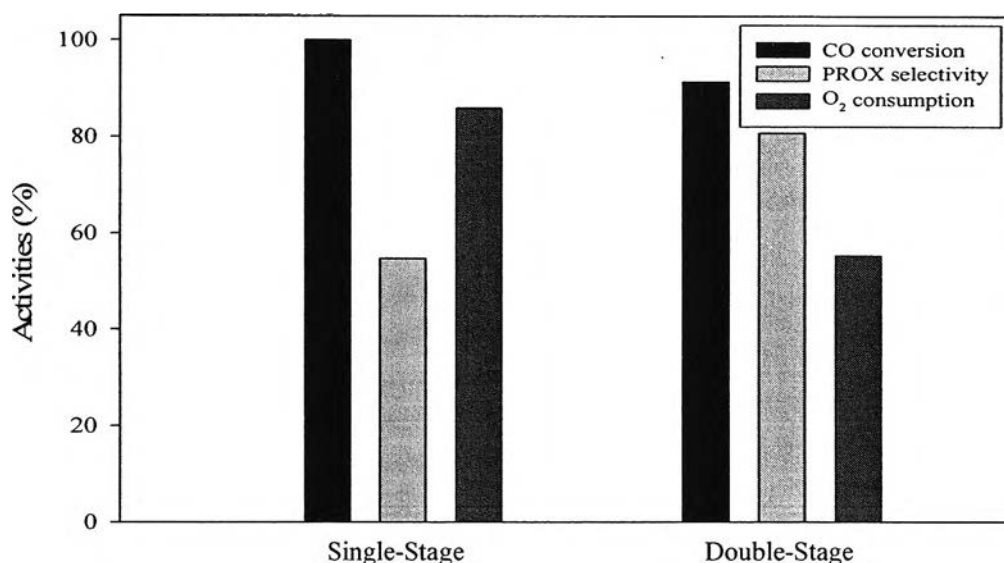
Figure 4.20 Comparison of activities of the single-stage and the double-stage processes. Conditions: 30°C and O_2 split ratio of 50:50.

From the previous results, the optimum operating conditions for the Au/TiO_2 catalyst in the double-stage reactors were identified at 50:50 O_2 split ratios, stage temperature of 30°C for both reactors, and 50:50 weight split ratios. The catalytic activity at the optimum operating condition in the double-stage reactors was compared with the catalytic activity operating in the single-stage reactor at 30°C, as shown in Figure 4.20.

The PROX selectivity could be seen to increase significantly from 54% in the single-stage, to 80% in the double-stage. The H_2 loss from the PROX reaction can be reduced. The concept is that in the double-stage reactor, a limited amount of O_2 is supplied for the first reactor in order to reduce CO concentration as much as possible. After that a massive amount of O_2 was fed into the second reactor to completely remove the surplus CO from the first reactor, so the oxygen consumption of the double-stage was less than the single-stage.

The double-stage reactor can reduce the consumption of O_2 when compared with the single-stage reactor. Luengnaruemitchai *et al.* (2007) deduced the same

findings that double-stage reactor can increase from 48% CO selectivity in the single-stage to 58% in the double-stage reactor. However, the single-stage provided a better CO conversion. Moreover, Ahluwalia *et al.* (2005) found that by increasing the number of reactors, the selectivity for CO oxidation can be enhanced. The results are in contrast with the results of Srinivas and Gulari (2006). Their percentage of the PROX selectivity for the double-stage operation was almost equal to that of the operation with the single-stage reactor at about 49%. Here, the O_2 is totally consumed for the reaction.

However, the CO conversion reduced by about 9% in the double-stage process, as shown in Figure 4.20. The explanation for this reduction is the different amounts of GHSV in the single-stage and double-stage reactor processing in Table 4.3. The GHSV of both processes are not equal because the double-stage process has the total amount of oxygen from the reactant mixture and is not the same as a single-stage, which is approximately 1%. The oxygen supply for both reactors is the fraction of total oxygen 1%. Moreover, the catalyst weight loading in the first and second reactor are about 0.05g, so the GHSV of the double-stage reactor processing is higher than the single-stage reactor processing, as shown the formula of GHSV in the equation below.

Snytnikov *et al.* (2008) applied Cu/CeO_2 for the PROX of CO reaction in a single-stage packed-bed reactor and varied the GHSV from 55,000 to 440,000 $cm^3h^{-1}g_{cat}^{-1}$. They proposed that when there was an increase in GHSV value, the capacity of the catalyst for CO oxidation was reduced.

$$GHSV = \frac{Mixture\ flow\ rate \times 60}{Catalyst\ weight}$$

Table 4.3 Gas hourly space velocity (GHSV) in the single and the double-stage processes

Single-Stage case	
GHSV of 1st reactor $(Cm^3 h^{-1} g_{cat}^{-1})$	30,000
Double-Stage case	
GHSV of 1st reactor $(Cm^3 h^{-1} g_{cat}^{-1})$	59,400
GHSV of 2nd reactor $(Cm^3 h^{-1} g_{cat}^{-1})$	60,000

4.3   Double-Stage Reactor with PROX Reaction in the Real Composition Reformate Gas

Finally, the 1%wt Au/TiO_2 catalyst was tested the catalytic activity for the PROX reaction with the real composition reformate gas. Commercial Cu-Zn/Al_2O_3 catalyst was used for methanol steam reforming reaction. The catalyst produced the reformate gas with the composition of 20% of CO_2 and H_2O, as shown in Figure 4.21 section of reforming. Then, the 1%wt Au/TiO_2 catalyst was used to lower the CO concentration in the real composition reformate gas with a double-stage reactor. The catalyst was operated at stage temperature of 30°C for both reactors, and 50/50 O_2 and weight split ratio which are the optimum operating conditions as operated in a double-stage reactor with simulate reformate gas. Figure 4.21 illustrates that the Au/TiO_2 can reduce the CO concentration by the PROX reaction in a double-stage reactor with 90% CO conversion and 27.32% PROX selectivity. According to Figure 4.21, the PROX reaction created more 1.1% of the CO_2 content from the converting of CO to CO_2. Moreover, the H_2 content outlet from the PROX reaction is almost the same as the H_2 content outlet from the reformate gas. Because, the double-stage reactor operating can reduce the H_2 loss from the PROX reaction (Srinivas and Gulari, 2006) However, the 1%wt Au/TiO_2 catalyst calcined at 200°C could not completely removed CO concentration from the real composition reformate gas. This happened because the real composition reformates gas contains approximately 20% of CO_2 and some amount of H_2O, but the simulated

reformate gas contains only 10% CO_2 and 10% H_2O. Therefore, the presence of CO_2 and H_2O in massive amounts from the real composition reformate gas are adsorbed on the catalyst surface and block the active site of the catalyst (Avgouropoulos *et al.*, 2006). However, testing of the PROX reaction with the real reformate gas composition can confirm that the Au/TiO_2 catalyst can be used to lower CO concentration in the H_2 rich steam from the reforming unit with the lowest CO content approximately 200 ppm.
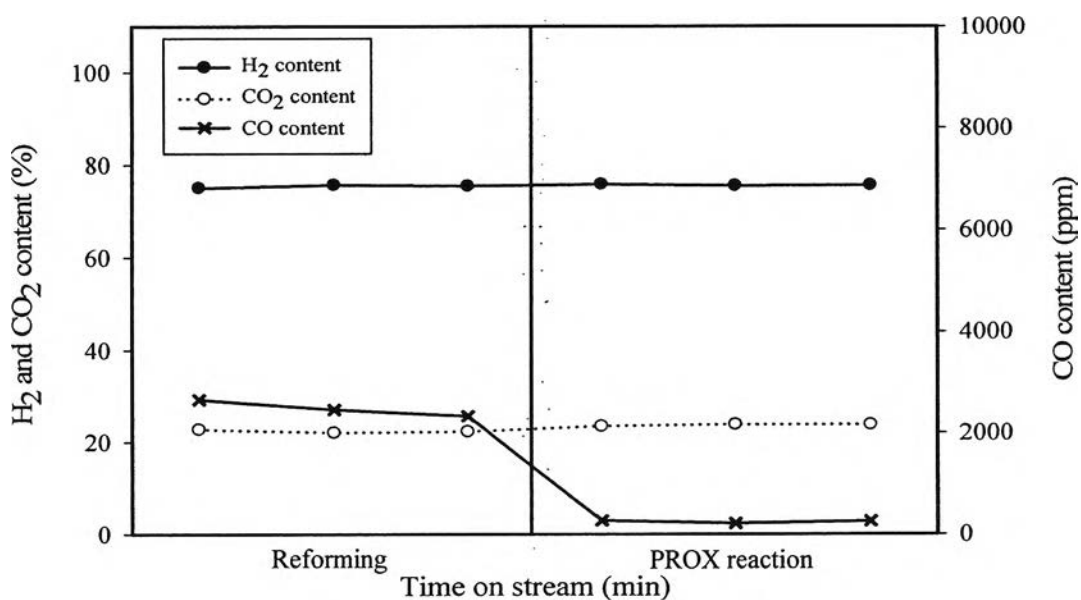

Figure 4.21 Gas composition of the reforming and PROX of CO reaction.